Solid-Liquid Separation after Liquid-Liquid Extraction. —Spectrophotometric Determination of Bismuth after Extraction of Its 2-mercaptobenzothiazole Complex with Molten Naphthalene—

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A new reagent, 2-mercaptobenzothiazole,sodium salt is described for the spectrophotometric determination of bismuth(II) after extraction of bismuth complex with molten naphthalene. This reagent reacts with bismuth(II) to form a water-insoluble complex. The complex is insoluble in chloroform or benzene, but easily soluble in molten naphthalene. The extracted mixture of bismuth complex and naphthalene is dissolved in dimethylformamide and the trace amounts of bismuth are determined spectrophotometrically. The linearity between the absorbance and bismuth concentration is held for 10 - 200 μg of bismuth in 10 ml of dimethylformamide. The molar absorptivity was calculated to be 1.1×10^4 $l \cdot mol^{-1} \cdot cm^{-1}$, the sensitivity 0.020 μg of bismuth per cm^2 for the absorbance of 0.001 and the relative standard deviation 0.76 % for ten times determinations.

1. Introduction

2-mercaptobenzothiazole, sodium salt reacts with bismuth(II) to form a water-insoluble stable complex. This complex is not extracted into organic solvents such as chloroform or benzene because of the low solubility, but easily extracted into molten naphthalene. The extracted mixture of the complex and naphthalene is separated from the aqueous solution , dissolved in dimethylformamide, and the trace amounts of bismuth is determined spectrophotometrically.

2. Experimental method

2.1 Apparatus

A Hitachi Model 200-20 double beam spectrophotometer was used for the absorbance measurements.

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A Toa-Dempa, Model HM-5A pH meter equipped with combined glass and calomel electrodes was used for pH measurements.

2.2 Reagents

Standard bismuth solution, 20 ppm. Prepared by diluting standard bismuth stock solution(1000 ppm) to 1000 ml with water.

2-mercaptobenzothiazole solution, 0.5 %. Prepared by dissolving 0.5 g of 2-mercaptobenzothiazole,sodium salt in 100 ml of water.

Buffer solution. Prepared by mixing suitable amounts of 1M ammonia water and 1M ammonium acetate solution, or 1M acetic acid and 1M ammonium acetate solution.

All other reagents used were of analytical grade and were used without further purification.

2.3 Procedure

Transfer 1 - 10 ml of 20 ppm standard bismuth solution to a 80 ml stoppered Erlenmeyer flask, and dilute with water to about 25 ml. Add 2.0 ml of the acetate buffer solution(pH 5.5) and 5.0 ml of 0.5 % 2-mercaptobenzothiazole solution. Mix well and warm the flask on a water bath at about 90 °C to precipitate the bismuth complex completely. Add 2.0 g of naphthalene and warm the flask in the water till naphthalene melts completely. Remove the flask from the bath and shake vigorously. Naphthalene will be solidified forming fine crystals suspended in the solution. Warm the flask at about 81 °C again and melt slowly the very fine crystals. Larger crystalline deposits will be grow up in the solution. Filter the mixture on a filter paper and wash with water. Remove the water clinging to the filter paper with a separate piece of paper. Spread the crystals on a dry filter paper for air-drying. Transfer them to a volumetric flask and add dimethylformamide so that the final volume becomes 10 ml. Mix well and measure the absorbance of the solution in a 10 mm cell against the reagent blank similarly prepared.

3. Result and discussion

3.1 Absorption spectra

Bismuth in the sample solution containing 5.0 ml of 20 ppm standard bismuth solution was extracted with molten naphthalene as bismuth-2-mercaptobenzothiazole complex at pH ca. 5.5. The mixture of the complex and naphthalene was dissolved in dimethylformamide, and the absorbance of the solution was measured at various wavelengths between 360 and 460 nm. The absorption spectra of the bismuth complex along with that of the reagent blank in naphthalene-dimethylformamide

solution are shown in Fig.1. The maximum absorbance occurs at 394 nm, at which the absorbance of the reagent blank is very small. Subsequent studies were therefore made at 394 nm.

3.2 Effect of pH on absorbance

The effect of pH on the absorbance of the bismuth complex in naphthalene-dimethylformamide solution was examined as shown in Fig. 2. It can be seen that the maximum and constant absorbance was obtained in the pH range 4.6 - 6.5 at 394 nm. An acetate buffer solution(pH 5.5) was found satisfactory in this pH region. Subsequent experiments were made at pH 5.5.

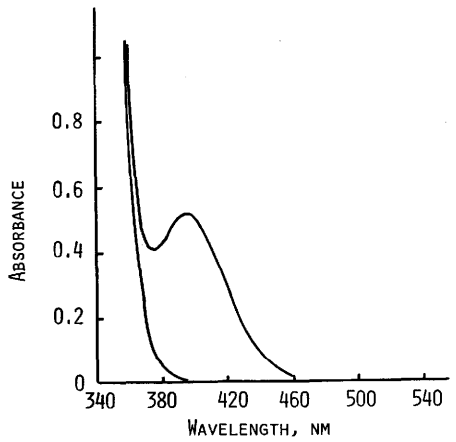

FIG. I ABSORPTION SPECTRA OF 2-MERCAPTOBENZOTHIAZOLE AND BISMUTH COMPLEX IN NAPHTHALENE-CHLOROFORM SOLUTION
BISMUTH : 100 µG ; 2-MERCAPTOBENZOTHIAZOLE : 2.0 G ; PH : 5.5 ; BUFFER SOLUTION : 2.0 ML
REFERENCE : WATER

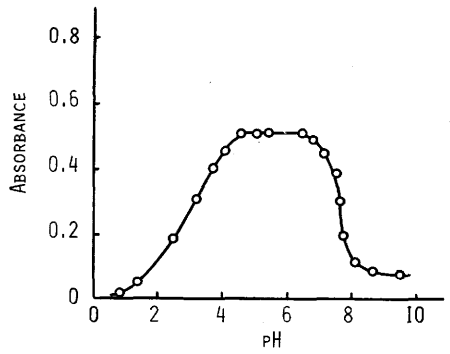

FIG. 2 EFFECT OF PH ON ABSORBANCE
BISMUTH : 100 µG ; 0.5% 2-MERCAPTOBENZOTHIAZOLE : 5.0 ML ; WAVELENGTH : 394 NM
REFERENCE : REAGENT BLANK

3.3 Effect of reagent concentration on absorbance

The effect of changes in the concentration of 2-mercaptobenzothiazole on the absorbance of the complex at pH 5.5 was examined at 394 nm. Fig. 3 shows that the absorbance increases by an increasing in the reagent concentration up to 2.0 ml of 0.5 % 2-mercaptobenzothiazole solution and becomes maximum with addition of 2.0 - 6.0 ml of it.

3.4 Effect of buffer solution on absorbance

The effect of addition of the acetate buffer solution(pH 5.5) on the absorbance was examined. As seen from Fig. 4, the addition of 0.5 - 5.0 ml of the buffer solution was practically without variation on the absorbance at 394 nm. For further study, 2.0 ml of the buffer solution were added.

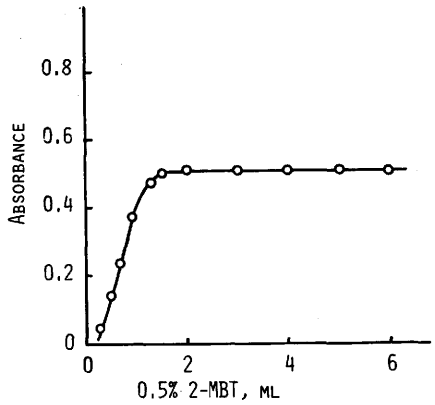

FIG. 3 EFFECT OF REAGENT CONCENTRATION ON ABSORBANCE
BISMUTH : 100 μG ; WAVELENGTH : 394 NM ; PH : 5.5 ; DIGESTION TIME : 15 MIN
REFERENCE : REAGENT BLANK

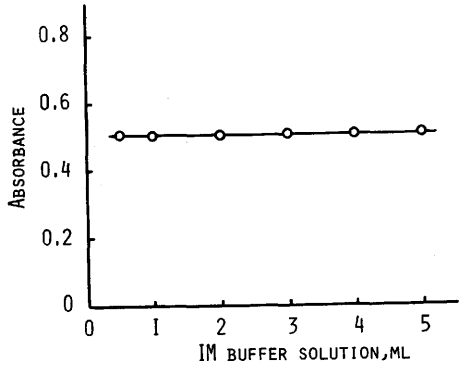

FIG. 4 EFFECT OF BUFFER SOLUTION ON ABSORBANCE
BI : 100 μG ; WAVELENGTH : 394 NM ; PH : 5.5 ; STANDING TIME : 10 MIN ; DIGESTION TIME : 15 MIN
REFERENCE : REAGENT BLANK

3.5 Effect of digestion time on absorbance

The bismuth complex in the solution containing 27 μg of bismuth was digested on a water bath at 90 °C and the extraction was carried out according to the recommended procedure. Fig.5 shows the effect of the digestion time on the absorbance. From these results, the complex was very stable at high temperature and the digestion for about 60 min had no effect on the absorbance of the complex.

3.6 Effect of naphthalene on absorbance

The bismuth complex was extracted from the solution with 0.5 -3.0 g of naphthalene under the optimum conditions and effect of the addition of naphthalene on the absorbance was tested. The result is shown in Fig. 6. This complex was very stable in molten naphthalene and almost completely extracted with the addition of 0.5 g of naphthalene. The rate of extraction of the complex into molten naphthalene was very rapidly because of high temperature. The extraction was completed with several times shaking.

3.7 Effect of standing time on absorbance

The effect of standing time of the complex in naphthalene-dimethylformamide solution was examined. The result is shown in Fig. 7. The color of the complex was stable and the absorbance remained constant.

3.8 Calibration curve

The bismuth complex obeyed Beer's law over the range 10 - 200 μg. The molar absorptivity was 1.1×10^4 $l \cdot mol^{-1} \cdot cm^{-1}$ at 394 nm and the sen-

sitivity was 0.020 μg Bi $cm^{-2}$for the absorbance of 0.001.

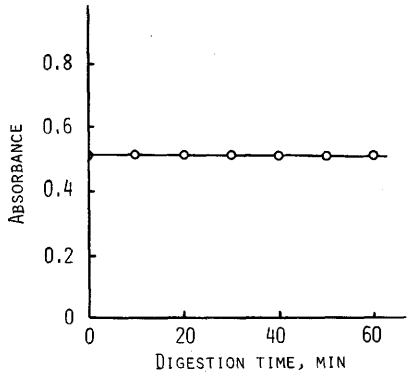

FIG. 5 EFFECT OF DIGESTION ON ABSORBANCE
BI : 100 μG ; PH : 5.5 ; BUFFER SOLUTION : 2.0 ML ; DIGESTION TIME : 15 MIN
REFERENCE : REAGENT BLANK

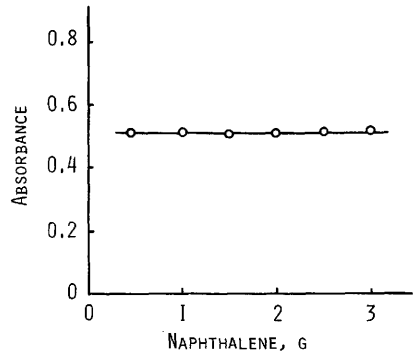

FIG. 6 EFFECT OF NAPHTHALENE ON ABSORBANCE
BISMUTH : 100 μG ; 0.5% 2-MERCAPTOBENZOTHIAZOLE : 5.0 ML ; PH : 5.5
REFERENCE : REAGENT BLANK

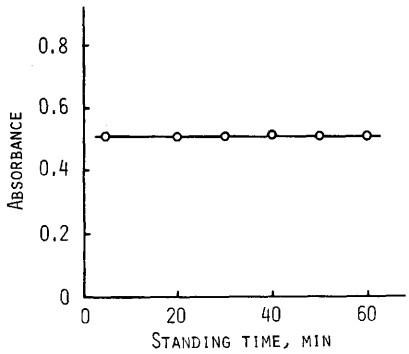

FIG. 7 EFFECT OF STANDING TIME ON ABSORBANCE
BI : 100 μG ; 0.5% 2-MERCAPTOBENZOTHIAZOLE : 5.0 ML ; WAVELENGTH : 394 NM ; PH : 5.5
REFERENCE : REAGENT BLANK

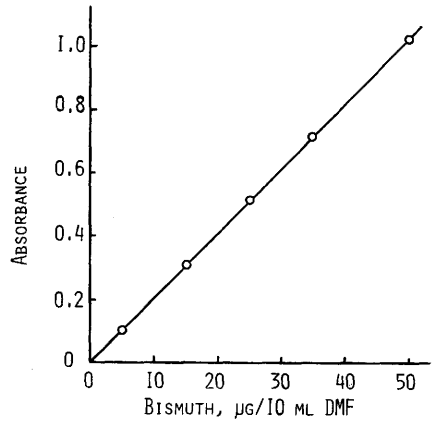

FIG.8 CALIBRATION CURVE FOR BISMUTH
WAVELENGTH : 394 NM ; PH : 5.5 ; 0.5% 2-MERCAPTOBENZOTHIAZOLE : 5.0 ML ; DIGESTION TIME : 15 MIN ; STANDING TIME : 10 MIN
REFERENCE : REAGENT BLANK

The precision of the method was tested by the measuring the absorbance of ten samples, each containing 27 μg of bismuth. The mean absorbance was 0.511 with a standard deviation of 3.90×10^{-3} (relative standard deviation 0.76 %)